

POLYALKYL HYDROBENZOINS

BY

MAURICE LESLIE WARD

B.A., University of Illinois, 1938

AN ABSTRACT OF A THESIS

**SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1942**

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ACKNOWLEDGMENT

The author expresses his sincere appreciation to Professor Reynold C. Fuson for his suggestions and encouragement during the course of this investigation.

He also wishes to thank the Abbott Laboratories for the Fellowship which he held for the year 1941-1942.

POLYALKYL HYDROBENZOINS

Section A

INTRODUCTION

The coupling of aromatic aldehydes with the binary mixture, magnesium-magnesium iodide, to prepare 1,2-glycols has been widely studied.¹ Since this reaction seems dependent upon steric factors arising from ortho substituents in the aldehyde, a study of the coupling of tipaldehyde* and 2,4-xylaldehyde was undertaken.

EXPERIMENTAL AND DISCUSSION OF RESULTS

Tipaldehyde and 2,4-xylaldehyde were prepared by a modified Gattermann reaction² from 1,3,5-triisopropylbenzene and *m*-xylene, respectively.

The binary mixture, magnesium-magnesium iodide, readily coupled 2,4-xylaldehyde to produce hydro- and isohydroxyloin. Hydroxyloin yielded *s*-di-*m*-xylylethane and *s*-di-*m*-xylyethylene when treated with hydriodic acid and phosphorus and iodine, respectively.

Although the zinc-copper couple was ineffective as a reducing agent for tipaldehyde, the binary mixture, magnesium-magnesium iodide, yielded the two isomeric hydrotipoints and *s*-ditipylethylene as the major products. The mode of formation of this unsaturated hydrocarbon is obscure.

These glycols were characterized by their diacetates and could be converted to *s*-ditipylethylene by the action of phosphorus and iodine, hydriodic acid or hydrobromic acid. The glycols were catalytically reduced over copper chromite to *s*-ditipylethane. This same hydrocarbon was produced by reducing *s*-ditipylethylene over Raney nickel. Either glycol could be converted to a similar mixture of ethylene dichlorides by

*For convenience of presentation the 2,4,6-triisopropylphenyl radical has been abbreviated to the *tipyl* radical. A corresponding condensation in nomenclature has been adopted, namely: 2,4,6-triisopropylbenzaldehyde is tipaldehyde, *s*-hexaisopropylhydrobenzoin is hydrotipoin, *s*-hexaisopropylidiphenylethylene is *s*-ditipylethylene, *s*-hexaisopropylbenzil is tipil, etc.

the action of phosphorus pentachloride in phosphorus oxychloride. These highly substituted dichlorides were unique in that they rapidly evolved hydrogen chloride gas at the melting point to yield *s*-ditipylacetylene.

SUMMARY

Tipaldehyde and 2,4-xylaldehyde were prepared from 1,3,5-triisopropylbenzene and *m*-xylene, respectively, by a modified Gattermann reaction. The binary mixture, magnesium-magnesium iodide, was a satisfactory reagent to couple these aldehydes to the corresponding substituted hydrobenzoin.

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Section B

INTRODUCTION

The dehydration of hydrobenzoin^{1,2} generally leads to the formation of desoxybenzoin or disubstituted acetaldehydes although much experimental work^{3,4} indicates that the products are enolic. A program of research was instituted to study steric hindrance as a possible means of stabilizing the enolic form.

EXPERIMENTAL AND DISCUSSION OF RESULTS

Dehydration of either hydrotipoin or isohydrotipoin with (a) sulfuric acid, (b) a mixture of glacial acetic acid-concentrated hydrochloric acid, (c) phosphorus pentoxide in benzene produced 2,2-ditipylvinyl alcohol. Distillation of isohydrotipoin *in vacuo* also produced this alcohol.

The alcoholic nature of the dehydration product was indicated by its ready formation of an acetate. The unsymmetrical nature of the molecule was established by cleavage to ditipyl ketone with either basic perhydrol or alkaline potassium permanganate. Ozonolysis of the vinyl alcohol led to tipoin rather than ditipyl ketone. Acidic reagents caused mi-

gration of one of the aryl groups to form molecules with a 1,2-ditipylethane carbon skeleton. Oxidation with chromic anhydride in glacial acetic acid produced tipil. Selenium dioxide reacted similarly to yield the diketone.

Attempted ketonization of the vinyl alcohol with methanol or ethanol saturated with dry hydrogen chloride failed to form the expected ditipylacetaldehyde or desoxytipoin. The product isolated has been assigned the structure of *s*-ditipylethylene oxide.

Reduction of the alcohol with hydriodic acid in glacial acetic acid yielded the known *s*-ditipylethylene, whereas high-pressure reduction in the presence of Raney nickel produced an isomeric alcohol. The structure of this pseudo reduction product has been designated as the *trans* form of 1,2-ditipylvinyl alcohol.

Desoxytipoin was acetylated by the addition of acetyl chloride to the mixture obtained by heating desoxytipoin with methylmagnesium iodide in dibutyl ether. Hydrolysis of this acetate regenerated desoxytipoin. The instability of the enol intermediate from the hydrolysis suggests that the acetate is best depicted as *cis*-1,2-ditipylvinyl acetate.

Dehydration of 2,2',4,4'-hydroxyloin with sulfuric acid produced 2,3,5,6-tetra-*m*-xylyldioxane. Dioxane formation by the dehydration of glycols is not new.⁵ Dehydration with a glacial acetic acid-concentrated hydrochloric acid mixture formed 2,2',4,4'-desoxyxyloin.

SUMMARY

Dehydration of hydrotipoin and isohydrotipoin formed a stable alcohol, which is best described as 2,2-ditipylvinyl alcohol. This vinyl alcohol was converted to an isomeric alcohol when it was subjected to high-pressure reduction in the presence of Raney nickel. *Trans*-1,2-ditipylvinyl alcohol best explains the chemical character of this molecule.

Desoxytipoin was acetylated. This acetate is represented as *cis*-1,2-ditipylvinyl acetate.

Dehydration of 2,2',4,4'-hydroxyloin with sulfuric acid and a glacial acetic acid-concentrated hydrochloric acid mix-

ture formed 2,3,5,6-tetra-*m*-xylydioxane and 2,2',4,4'-desoxyxyloin, respectively.

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VITA

The author was born near Rock Falls, Illinois, on August 25, 1917. He attended elementary school in Whiteside County. He attended Chaffey Union High School, Ontario, California, for two years and was then graduated from the Rock Falls Township High School, Rock Falls, Illinois in 1934. He entered Carthage College, Carthage, Illinois, which he attended for three years. He was granted the degree of Bachelor of Arts from the University of Illinois in June, 1938, and in the fall of the same year he entered the graduate school of the University of Illinois as a teaching assistant in inorganic chemistry, which position he held for three years. He held the Abbott fellowship during 1941-1942.



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